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Re: 6495-100341

To Whom It May Concern:

This is to certify that a professional translator on our staff who is skilled in the French language translated the enclosed French Patent No. 117028 from French into English.

We certify that the attached English translation conforms essentially to the original French language.

Kim Vitray
Operations Manager

Subscribed and sworn to before me this 15th day of November, 2004.

Tina Wuelfing
Notary Public

My commission expires: December 8, 2007

EXCELLENCE WITH A SENSE OF URGENCY®



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METHOD FOR THE MANUFACTURE OF PIECES MADE OF ALLOY STEEL AND
PIECES OBTAINED BY THIS METHOD

Patent Holder:	Joint Stock Company known as: SOCIÉTÉ DES FORGES ET ATELIERS DUE CREUSOT residing in France (Seine).
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The invention concerns the manufacture of pieces made of alloy steel. In particular, its purpose is the manufacture of pieces with high mechanical properties of resistance to stress corrosion cracking in a humid environment in the presence of hydrosulfuric acid.

In bore holes in oil and natural gas fields, for example, the tubes that are used can come in contact with the humid and hot medium which is laden with hydrosulfuric acid under pressure. In addition, the steel pieces of the installations for processing oil products or natural gases can come in contact with a liquid or gaseous medium which is practically saturated with hydrosulfuric acid under pressure at temperatures which are usually higher than ambient temperature.

These conditions are very disadvantageous for steels, and within a varying period one can see cracking due to the superposition of mechanical stresses and embrittlement caused by hydrogen originating from the corrosion by hydrosulfuric acid.

It has been noted that the cracks originate most of the time from an insufficiently stable metal structure, where the metal notably comprised incompletely converted martensite or residual austenite dispersed in the mass.

In addition, especially for bore hole applications in the oil fields, it is essential to obtain steels having sufficiently high mechanical properties.

To resist cracking, steels have been tested that until now have proved difficult to use, and in particular, difficult to work. Moreover, it remains difficult to achieve high mechanical properties.

The invention allows the production of a steel having satisfactory mechanical properties with perfect resistance to cracking in the presence of even hydrosulfuric acid under pressure and at temperatures above ambient temperature.

It has been noted that it was possible to use a steel of the chromium-molybdenum-vanadium type, which until now had been reserved for other fields, provided that one used a treatment especially chosen for the conditions of use that have been specified.

According to the invention, the method consists in using a steel having the following composition by weight:

C%, 0.10-0.25;

Si%, 0.10-0.50;

Mn%, 0.30-1.0;

Cr%, 1-14;

Mo%, 0.4-1.5;

V%, 0.10-0.60;

Ni%, 0-1,

and in the thermal treatment in two steps of this steel, the first step consisting of an austenization at a temperature of 975-1100°C, followed by a cooling (quenching) at an average rate equal to at least 30°C per minute from 850 to 600°C, and the second step consists of tempering at a temperature of 725-800°C to obtain pieces having a yield strength of 55-65 kg/mm².

According to the invention, one thus uses a tempering steel which is capable of withstanding tempering at high temperature while preserving high mechanical properties and while assuming a thermodynamically stable structure, as required to provide resistance to corrosion under tension.

The invention will now be described in greater detail with reference to special examples.

Example 1. – Test pieces were prepared from steel having the following composition by weight:

C%, 0.17;

Si%, 0.30;
Mn%, 0.50;
Cr%, 2.5;
Mo%, 1;
V%, 0.25;
Ni%, 0.2.

This steel is intended to come in contact with a saturated solution of hydrosulfuric acid.

It was subjected to the following treatment:

First step of the treatment: austenization at a temperature of 980°C for 1 h, following by cooling in the air (quenching);

Second step of the treatment: tempering at a temperature of 750°C for 1 h.

The mechanical properties achieved are as follows:

Yield strength $E = 62 \text{ kg/mm}^2$;

Tensile strength $R = 72 \text{ kg/mm}^2$;

Elongation $A = 24\%$ (effective length of the test piece equal to four times the diameter).

The structure of the steel which has been treated in this manner consists of finely spheroidized carbides that are regularly distributed on a ferrite base which no longer contains any area of free ferrite. This structure is clearly demonstrated by attack using a solution of picric acid in alcohol.

Steel which has been treated in this manner has been tested in contact with a saturated solution of hydrosulfuric acid containing 0.5% by volume of acetic acid, the purpose of the latter being to accelerate and worsen the corrosion. The metal must be placed in circular bending, where the maximum stress is slightly greater than the yield strength of the bent metal. No cracking was observed after 3000 h of this treatment.

In contrast, at tempering temperatures below 725°C, or for tempering that is too short and confers to the metal a yield strength greater than 65 kg/mm^2 , one obtains failures in less than 500 h.

Example 2. – Tubes were produced made of a steel having the following composition:

C%, 0.14;
Si%, 0.14;
Mn%, 0.45;
Cr%, 2.49;
Mo%, 0.90;
V%, 0.22.

These tubes are intended for the exploitation of oil wells whose gases contain a proportion of 15-20% by volume of hydrosulfuric acid.

The tubes were subjected to the following treatment:

First step of the treatment: austenization at a temperature of 1000°C for a duration of 4 min in a continuous furnace. The cooling was performed with water.

Second step of the treatment: tempering at a temperature of 750°C for 1 h.

The mechanical properties obtained are as follows:

Yield strength $E = 60 \text{ kg/mm}^2$;

Tensile strength $R = 69 \text{ kg/mm}^2$;

Elongation $A = 25\%$ (test pieces made from the steel of the tubes having an effective length equal to four times the diameter).

The structure of the steel is similar to that indicated by Example 1.

Test pieces produced from the metal of the tubes of the present example and having been subjected to the same treatment were subjected to the tests described in Example 1, and no cracking was observed after 3000 h.

Example 3. – Test pieces were produced from steel having the following composition by weight:

C%, 0.20;

Si%, 0.23;

Mn%, 0.52;

Cr%, 11.5;

Mo%, 1.10;

V%, 0.30;

Ni%, 0.40.

This steel is intended to come in contact with a saturated solution of hydrosulfuric acid.

The high content of the chromium of this steel is intended to improve its resistance to general corrosion, that is to decrease the loss of thickness of the pieces during use.

The steel was subjected to the following treatment:

First step of the treatment: austenization at a temperature of 1000°C for 15 min followed by cooling in the air;

Second step of the treatment: tempering at a temperature of 775°C for 1 h.

The mechanical properties obtained are as follows:

Yield strength $E = 61 \text{ kg/mm}^2$;

Tensile strength $R = 82 \text{ kg/mm}^2$;

Elongation $A = 25\%$ (effective length of the test piece equal to four times the diameter).

The structure of the steel is similar to that indicated for Example 1.

The steel thus treated was tested as provided for in Example 1, and no cracking was observed after 3000 h.

It should be understood that the examples which have just been given were intended to specify special cases of embodiment of the invention. However, the treatment temperatures and times indicated therein can always vary.

As far as the austenization temperature is concerned, it should vary only between 975 and 1100°C. As far as the tempering temperature is concerned, it should vary only from 725 to 800°C.

The choice of the temperatures to be used, preferably between these limits, as well as the tempering time, must take into account the desired yield strength of 55-65 kg/mm².

Finally, in the preceding examples, it has been indicated that the cooling was carried out either with air (Examples 1 and 3) or with water (Example 2). The choice of the cooling means used obviously depends on the shape and the thickness of the pieces, because the cooling must be sufficiently rapid to ensure the quenching of the steel.

Claims

The object of the invention consists of:

1. A method for the manufacture of pieces made of alloy steel, capable of resisting stress corrosion cracking in a humid environment which is laden with hydrosulfuric acid, possibly under pressure, and possibly at a temperature above ambient temperature, characterized by the following points, considered separately or in combination.

a. The method comprises the use of a steel having the following composition by weight: C%, 0.10-0.25; Si%, 0.10-0.50; Mn%, 0.30-1.0; Cr%, 1-14; Mo%, 0.4-1.5; V%, 0.10-0.60 and Ni%, 0-1, and the thermal treatment in two steps of the steel; the first step consists of an austenization at a temperature of 975-1100°C followed by cooling at a rate equal to at least 30°C per minute from 850 to 600°C, and the second step consists of tempering at a temperature of 725-800°C to produce pieces having a yield strength of 55-65 kg/mm²;

b. The steel used has the following composition by weight: C%, 0.17; Si%, 0.30; Mn%, 0.50; Cr%, 2.5; Mo%, 1; V%, 0.25; Ni%, 0.2;

c. The steel used has the following composition by weight: C%, 0.14; Si%, 0.14; Mn%, 0.45; Cr%, 2.49; Mo%, 0.90; V%, 0.22;

d. The steel used has the following composition by weight: C%, 0.20; Si%, 0.30; Mn%, 0.60; Cr%, 11.5; Mo%, 1.10; V%, 0.35; Ni%, 0.40;

e. The first step of the thermal treatment consists of an austenization at a temperature of 980-1000°C for approximately 1 h, followed by a cooling;

f. The first step of the thermal treatment, more especially for the case of tubes, consists of an austenization at a temperature of 1000-1050°C for a duration of 1 to 5 min;

g. The second step of the thermal treatment consists of tempering at a temperature of approximately 750°C for approximately 1 h.

2. As novel industrial products, the pieces, and, in particular, the tubes, produced by the method according to Claim 1.